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Effects of Urbanization on Organic Carbon Loads in the Sacramento River, California

J. O. Sickman,[1] M. J. Zanoli,[2] and H. L. Mann[3]

[1]   To gain better understanding of the effects of urbanization on organic matter transport in rivers, we quantified total organic carbon loading from point and non-point urban sources within the metropolitan area of Sacramento and compared these loads to the amount of organic carbon carried in the downstream Sacramento River. Median total organic carbon (TOC) concentrations in the Sacramento River, non-point urban runoff and wastewater treatment plant effluent were 2.1, 8.9, and 23 mg L^{-1}, respectively. Dissolved organic carbon (DOC) in non-point runoff and the river had similar specific UVA absorbance and disinfection by-product formation potential, but based on radiocarbon measurements, non-point DOC was substantially older (age > 2000 a) than DOC in the Sacramento River. This finding suggests that DOC in non-point runoff is derived primarily from leaching of older soil organic matter. The 10th, 50th, 90th and 99th percentile contributions of urban sources to daily TOC load in the Sacramento River were 10%, 20%, 38% and 80%, respectively. Total urban TOC yield was 150 kg $ha^{-1}yr^{-1}$ and urban sources contributed ~17% of the annual load of TOC in the Sacramento River below Sacramento.

Citation: Sickman, J. O., M. J. Zanoli, and H. L. Mann (2007), Effects of Urbanization on Organic Carbon Loads in the Sacramento River, California, *Water Resour. Res.*, *43*, W11422, doi:10.1029/2007WR005954.

1.   Introduction

[2]   Organic matter is an ubiquitous component of surface waters and its chemical composition and concentration influences many critical biogeochemical processes in rivers [*Findlay and Sinsabaugh*, 2003]. Riverine dissolved organic carbon (DOC) is primarily composed of humic and fulvic substances derived from soil organic matter, which are recalcitrant and hydrophobic [*Thurman*, 1985]. DOC contributes energy to aquatic foodwebs through uptake by microbes [*Tranvik*, 1992] and abiotic processes that produce bioavailable particulate organic carbon (POC) from DOC (flocculation and sediment adsorption) [*Eisma and Cadee*, 1991; *McKnight et al.*, 2002]. Total organic carbon (TOC = DOC plus POC) influences light attenuation in rivers with effects on primary productivity and autochthonous DOC production [*Morris et al.*, 1995]. The areal yield (i.e., mass per catchment area per time) of organic compounds in rivers ranges from less than 3 to greater than 130 kg ha^{-1} yr^{-1} [*Aitkenhead and McDowell*, 2000]. Global models suggest that about 170 teragrams C yr^{-1} of riverine organic carbon are delivered to the oceans [*Harrison et al.*, 2005], which is approximately 25% of annual terrestrial net ecosystem production (NEP; 800 Tg C yr^{-1}; *Xiao et al.* [1998]).

Hence understanding of processes generating and consuming riverine organic carbon is needed to assess how ecosystems are responding to environmental change at both local and global scales [*Bellamy et al.*, 2005; *Freeman et al.*, 2001a].

[3]   In many regions, conversion of natural landscapes to agriculture and urban areas is altering the quantity and composition of organic matter delivered to rivers with adverse effects on ecosystems and society. Conversion of natural wetlands and grasslands to agricultural uses has substantially altered the Sacramento-San Joaquin Delta (Delta) of California during the 20th Century [*Jassby and Cloern*, 2000]. Inputs of dissolved organic carbon (DOC) from terrestrial sources have increased through oxidation of soil organic matter following the introduction of agriculture, while TOC derived from internal sources such as phytoplankton has been reduced due to decreasing aquatic primary productivity in the Delta [*Jassby et al.*, 2002]. Additional organic carbon sources associated with urbanization include municipal wastewater discharges, and non-point runoff carrying a variety of petrochemicals. These changes in organic carbon sources have likely lowered the overall productivity of the Delta ecosystem and may be partially responsible for recent declines in pelagic fish populations [*Hieb et al.*, 2005].

[4]   Waters from the Sacramento River constitute about 80% of the flow to the Delta, the San Joaquin River about 10-14%, and smaller tributaries to the east provide the remainder [*California Department of Water Resources*, 2001]. On a daily basis, rivers supply about 68% of the daily load of TOC to the Delta; the remainder comes from autochthonous production and agricultural drainage from Delta islands (mean daily TOC input is ~393 megagrams

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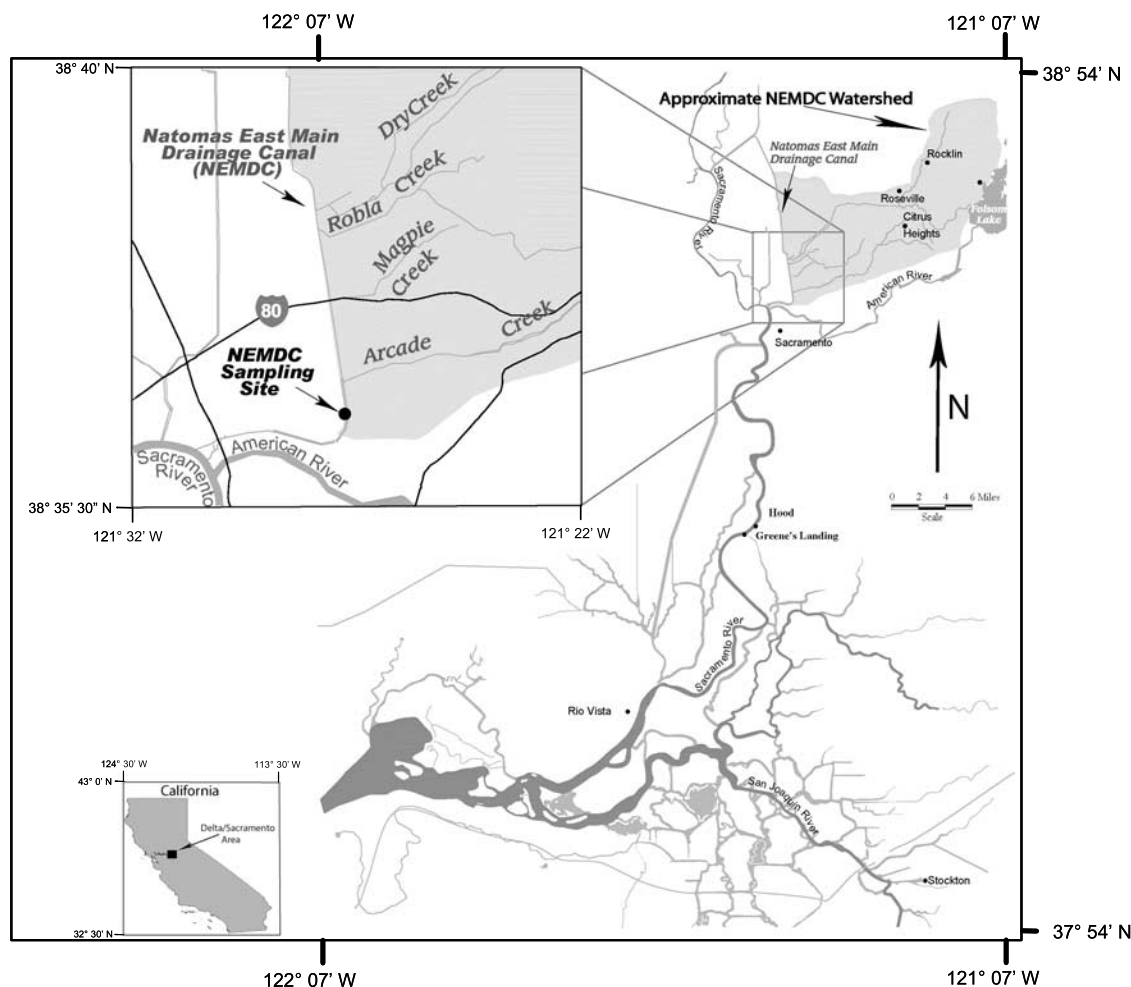
Figure 1. Map of the Sacramento Metropolitan Area, the Natomas East Main Drainage Canal (NEMDC) watershed and the Sacramento-San Joaquin Delta.

day^{-1}; *Jassby and Cloern*, [2000]). Thus on an annual basis the Sacramento River is the single largest input of TOC to the Delta [*Tetra Tech Inc.*, 2006] and much of this riverine TOC load reaches the intake pumps for the California State Water Project (SWP) located in the southern Delta. The SWP supplies drinking water to 22 million people in central and southern California. Particulate and dissolved organic carbon found in Delta exports are known to form disinfection by-products (DBPs) during drinking water treatment processes [*California Department of Water Resources*, 2001]. DBPs include suspected carcinogens such as trihalomethanes which are regulated under the U.S. Safe Drinking Water Act. Given the importance of the Sacramento River in supplying DBP precursors to the Delta and SWP, better quantification of TOC sources within the Sacramento River watershed are needed if effective source-control programs are to be developed.

[5] During the last two decades, substantial population growth has occurred in the city of Sacramento and its suburbs. Large-scale conversion of agricultural lands to urban uses has occurred, however, there are few data with which to assess the impact of these changes on aquatic ecosystems and drinking water quality. Thus the main objective of our study was to quantify hydrologic fluxes of organic carbon from urban areas surrounding Sacramento and evaluate whether these inputs are a major source of organic carbon and DBP precursors in downstream reaches of the Sacramento River. A secondary objective was to identify sources of organic carbon in urban runoff. We report results from a six-year investigation (1999–2005) of the Natomas East Main Drainage Canal (NEMDC). The NEMDC watershed drains a predominantly urban landscape within the greater Sacramento Metropolitan Area and its waters enter the Sacramento River near downtown Sacramento (Figure 1). The NEMDC watershed is rapidly urbanizing with population growth rates among the highest in the State of California [*California Department of Water Resources*, 2001]. We combined regional estimates of non-point source TOC loading with point-source inputs from Sacramento's main wastewater treatment plant to estimate total urban loading of TOC to the Sacramento River. In addition, we made measurements of the isotopic composition, chemical structure and reactivity of urban DOC to gain better understanding of its sources and reactivity with chlorine. Our investigation represents one of the most complete studies of urban runoff in California and provides data to help estimate

Table 1. Watershed Characteristics of Study Sites and Nearby Catchments

			Landuse Percentage		
Watershed	Watershed Area, km^2	Elevation Range, m asl	Urban	Agriculture	Other[a]
NEMDC	466	7 – 305	59%	7%	34%
Arcade Creek	87	10 – 84	90%	0%	10%
Sacramento Metropolitan Area	1,424	3 – 122	30%	29%	41%
Sacramento River at Freeport[b]	59,570	0 – 4, 322	3%	14%	83%

[a]Other includes forest, rangeland, wetlands, water, shrublands and rock.
[b]Data from *Saleh et al.* [2003].

how regional organic carbon dynamics in California and elsewhere may be changing in response to urbanization.

2. Materials and Methods

2.1. Land Use Patterns in the Sacramento River Watershed

[6] The NEMDC gaging station was located at the El Camino Road bridge about 5 km above the canal's confluence with the Sacramento River and was selected as our project site because it carries urban runoff from about one-third of the Sacramento Metropolitan Area (SMA) (Figure 1). The NEMDC watershed is 466 km^2 in area and ranges in elevation from 7 - 305 m above-sea level (Table 1). Landuse in the NEMDC watershed is predominantly urban (59%) with a small amount of rice acreage (7%) and substantial undeveloped areas (34%). A previously studied subcatchment, Arcade Creek, contains the most highly developed land area within the NEMDC watershed with 90% urbanization [*Saleh et al.*, 2003]. For the entire SMA (1424 km^2) about 30% of the land area is urbanized with the remaining area split between agricultural and undeveloped lands. Snowmelt from protected lands in the Sierra Nevada mountains supplies most of the runoff to the upper Sacramento River watershed with developed lands making up less than 20% of the 59,570 km^2 river basin.

2.2. Hydrological Data at NEMDC

[7] In this paper, annual fluxes of water and organic carbon are defined on a year that runs from 1 July through 30 June of the following year (e.g., fluxes for year 2002 = 1 July 2001 through 30 June 2002). Rainfall data from twelve stations in the SMA were used to determine the timing of rainfall events in the NEMDC watershed. From 1999 through late 2004, a wire-weight gage was used to periodically measure stage at the NEMDC gaging station. These measurements were used in conjunction with a continuous record of stage recorded at Arcade Creek near its confluence with NEMDC. At Arcade Creek stage readings were made every 60 seconds using a pressure transducer and recorded when the stage change was greater than 1.52 cm. Linear regressions were developed between NEMDC stage and Arcade Creek stage using paired data for individual years (2000 through 2004); the coefficients of determination for these equations were ≥0.98. Using these equations we developed a continuous record of stage at NEMDC from 1 July 2001 through 20 June 2004, and 21 October 2004 through 9 December 2004. From 21 June 2004 through 20 October 2004, the Arcade Creek gage

was not operating properly and we instead used the wire-weight gage to estimate NEMDC stage. Wire-weight gage measurements were made approximately monthly and values extrapolated to the midpoint of the time-interval between measurements. NEMDC discharge during the summer and early autumn of 2004 was extremely low, stage varied by less than 0.15 ft and there were no rain events, hence monthly measurements adequately captured the stage variations.

[8] From 9 December 2005 through 30 June 2005, a bubble gage and data logger were installed at NEMDC to record stage at 15 minute intervals. Periodic measurements of stage using the wire-weight gage continued after the installation of the bubble gage to insure continuity of stage measurements over the 2001–2005 study period. Coefficients of determination among the three stage recording devices were ≥0.97 after December 2004.

[9] A rating curve was developed for the NEMDC gaging station from stage readings and discharge measurements. Discharge measurements were made by the velocity area method using both a Price AA flowmeter and a SonTek Acoustic Doppler Profiler (ADP) unit. The rating curve was developed with replicate discharge measurements made at 27 stage heights; these measurements spanned the full range of stages encountered at NEMDC during the study.

2.3. Chemical Analysis of Grab Samples

[10] Grab samples for organic carbon analysis were collected on approximately a monthly basis at NEMDC and at the Hood water quality station on the Sacramento River between July 1999 through June 2005. Hood Station is located approximately 32 km downstream of the city of Sacramento. Additional water samples were collected at NEMDC on days with >2 cm precipitation or on rain-days following prolonged periods without precipitation (i.e., first flush storms). During the study, 83 grab samples were collected at the NEMDC gaging station using a 10-liter stainless steel bucket and wire cable. The bucket was rinsed three-times with deionized water and once with sample water before samples were collected. The median time interval between samples at NEMDC was 15 days during years 2002–2005 (range = 1 to 41 days). All grab sample data used in this study are available in an online database (Water Data Library) operated by the Department of Water Resources (http://wdl.water.ca.gov/includes/station_details.cfm?qst_id = 1362). This database also includes co-collected major ion and nutrient data from NEMDC which will be published in the near future.

[11] All organic carbon analyses of grab samples were performed at the Bryte Analytical Laboratory operated by the California Department of Water Resources. Documentation describing quality control and quality assurance procedures used in the laboratory can be accessed at http://www.wq.water.ca.gov/qaqc/qaqcpubs.cfm. For TOC, unfiltered sample was placed into 40 mL amber bottles (I-Chem series 200) and acidified to pH 2 using phosphoric acid to preserve the sample and remove inorganic carbon. Filtered samples for DOC analysis were prepared by passing water through 0.45 μm polycarbonate membrane filters and into 40 mL amber bottles (I-Chem series 200) using a stainless steel filter holder and peristaltic pump. Filters and tubing were rinsed with a minimum of 1 liter of 18 megaohm deionized water prior to use. DOC samples were acidified to pH 2 using phosphoric acid. TOC and DOC analyses were performed using a Shimadzu TOC 5000A TOC analyzer (high temperature combustion: EPA Method 415.1). The mean ratio of DOC:TOC at NEMDC was 0.75 ± 0.17 (S.D.).

[12] Analytical accuracy of DOC and TOC measurements was assessed by spike recoveries and incorporation of standard reference material in each analytical run at a 5% frequency. Overall precision of laboratory TOC measurements was better than ±30% and accuracy was between 80–120%. Procedural blanks were run for both TOC and DOC and mean values were 0.1 ± 0.01 mg L^{-1} and 0.2 ± 0.02 mg L^{-1}, respectively; both values are below the detection limit of the TOC analyzers.

[13] The potential for DOC to form disinfection by-products was assessed in filtered river and urban runoff samples by two measures. In the first, we measured absorbance of light at 254 nm in a 1 cm quartz cuvette on a laboratory spectrophotometer. Specific UVA absorbance (SUVA) was computed by dividing absorbance by DOC concentration in mg L^{-1} and multiplying by 100. In the second measurement, dose-based, total trihalomethane formation potential was estimated using a method developed by the California Department of Water Resources [Chow et al., 2006]. The assay measured trihalomethane formation in unfiltered water samples over a 7 day incubation at 20°C following the addition of sodium hypochlorite (final chlorine concentration = 120 mg L^{-1}). Solutions were buffered to a pH of 8.3 with H_3BO_3 and at the end of the incubations remaining free chlorine was quenched by addition of sodium sulfite. Extraction and measurement of trihalomethane species, principally chloroform, were accomplished using a purge and trap collector interfaced with an HP 5890 II gas chromatograph following EPA Method 524.2.

[14] On two dates, 8 November 2002 and 28 April 2003, large volume samples were collected at NEMDC for isolation of DOC for radiocarbon dating. Samples were filtered as described above into 4 liter glass bottles that had been combusted at 500 °C for 3 h. In the lab, samples were acidified to pH 2 and then rotary evaporated to dryness under vacuum at 40°C. The solid material remaining contained the DOC of the sample along with salts. Samples were combusted in evacuated quartz tubes with CuO and the resultant CO_2 was purified and isolated cryogenically on a vacuum extraction line. The CO_2 samples were then reduced to graphite at high temperature in the presence of H_2 and formed into graphite targets for ^{14}C measurement by accelerator mass spectrometry [Vogel et al., 1987]. Samples were analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. Radiocarbon concentrations are reported as a fraction of modern carbon (fmc) relative to a 1950 atmospheric CO_2 ^{14}C standard [Stuiver and Polach, 1977]. Method precision averaged 0.02 fmc for field duplicates.

2.4. Flow Measurements and TOC Concentrations in the Sacramento River

[15] Daily discharge data were obtained from a U.S. Geological Survey gaging station on the Sacramento River at Freeport, which is located approximately 16 km downstream of Sacramento. Since no major tributaries join the Sacramento River between Freeport and Hood Station, flows at Hood closely approximate flows upstream at Freeport.

[16] From 1 July 2001 through 7 April 2002, TOC concentrations in the Sacramento River at Hood Station were measured using weekly grab samples. Beginning 8 April 2002, TOC concentrations were made, in situ, with a Shimadzu TOC 4100 on-line analyzer (high temperature combustion method) [Sickman et al., 2005]. Real-time data for Hood Station are available on the California Data Exchange Center website, http://cdec.water.ca.gov, under the station code SRH. River water was supplied to the analyzer by a submersible pump kept at a constant inlet depth of 1-meter using a hose reel and float system. Mean daily TOC concentrations were computed from on-line replicated measurements of TOC made every hour (average of 72 measurements per day). During short periods when the analyzer was down for repairs or service, we linearly interpolated mean daily TOC to fill in gaps in the record. Overall data capture for the 2001-2005 period was better than 96% (>10^5 TOC measurements). The mean ratio of DOC:TOC (by laboratory combustion analysis) at Hood Station was 0.78 ± 0.12 (S.D.) during 2001-2005. To our knowledge this is the first example of real-time measurements of riverine TOC made in the United States and it represents the most intensive measurements of TOC concentration in the Sacramento River available.

2.5. Calculation of TOC Loads

[17] Relatively few NEMDC samples were collected during 1999 and 2000, and real-time monitoring of TOC at Hood Station was not fully operational until Spring 2002. Thus we present loading estimates for years 2002 through 2005 only. However, all of the chemical and hydrologic data collected during 1999–2005 were used in modeling of TOC loads at NEMDC.

[18] We used 77 of the 83 NEMDC samples to develop our primary predictive models of concentration and load described below. Six of the samples were excluded from the primary models because they were collected during first flush storms that had different discharge:concentration and discharge:load relationships than the overall data set (Figures 2a, 2b and 3a). Instead, a secondary, first flush model, described in section 2.6 below was used to model TOC concentrations and loads during first flush storms. For years 2002–2005 the first flush model was used on 18 days.

[19] Hydrologic loads of river-borne materials can be computed as the integral of the product of instantaneous
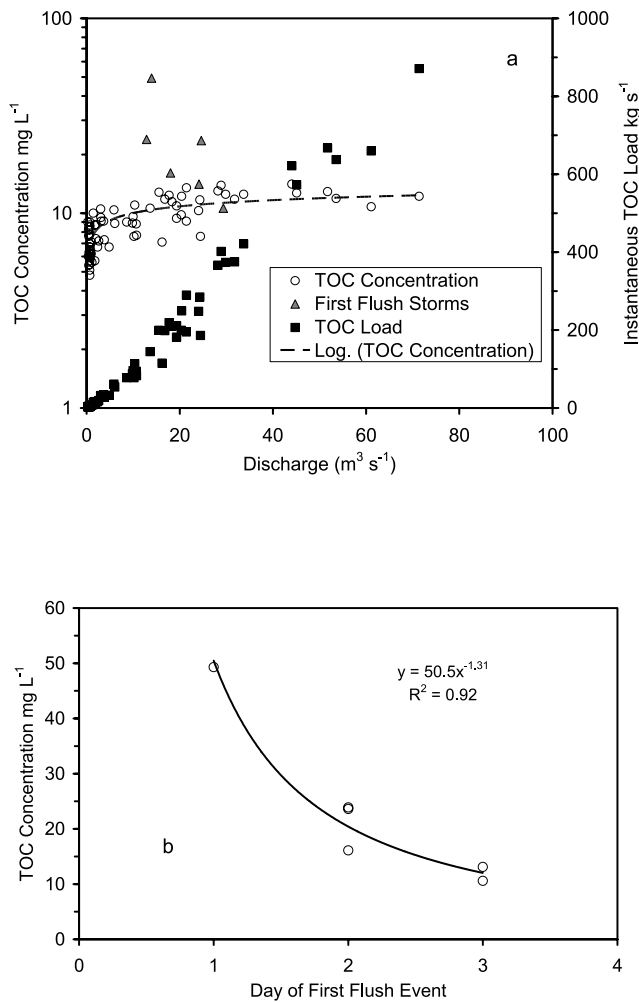
Figure 2. Panel a: relationship among instantaneous discharge and TOC concentration (open circles) and instantaneous TOC load (solid squares) at NEMDC. First flush storms are shown (solid triangles). Panel b: model describing the exponential decline in TOC concentrations during first flush storms in Sacramento, California (NEMDC watershed).

discharge and concentration between a defined time interval (*dt*):

$$L = \int_0^t Q \cdot C \, dt \qquad (1)$$

where, L is the total load in the time interval 0 to t; Q is the instantaneous discharge and C is the instantaneous concentration of a material. In practice discharge can be measured at short time steps (e.g., daily to hourly) using automated gaging equipment, however chemical measurements are typically made over weekly or longer timescales. In the Sacramento River, real-time measurements of TOC, made after April 2002, allowed us to directly use equation 1 on a daily time step to compute TOC loads in the river. For daily loads at NEMDC we used multiple approaches to model TOC concentrations and loads from periodic chemical samples and continuous discharge records. Multiple approaches were used in order to assess the best method

for computing TOC loads given the flashy nature of discharge in the NEMDC watershed.

[20] The first method we used was simple extrapolation of measured TOC to the midpoint between sampling dates or to the most recent substantial discharge change to generate a daily record of TOC concentrations [*Coats et al.*, 2002]. Loads computed by this interpolation method, also known as a worked record, can be accurate to within ±15% [*Sickman et al.*, 2001]. Daily TOC concentrations from the worked record were then multiplied by daily discharge to compute daily TOC flux and summed over longer time periods. This method was used for computation of daily TOC loads in the Sacramento River between 1 July 2001 and 7 April 2002 and at NEMDC for years 2002– 2005.

[21] The Beale's ratio estimator was the second method we employed at NEMDC to compute daily TOC loads [*Beale*, 1962; *Tan*, 1965]. The method assumes a constant ratio between concentration and discharge. Discharge-weighted mean concentration was multiplied by total discharge in the defined time interval, and the result adjusted using a factor that incorporates the ratio of the covariance of load with discharge to the variance of discharge [*Cohn*, 1995]. To improve the accuracy of loads computed using the Beale's ratio estimator, data were stratified by flow-class
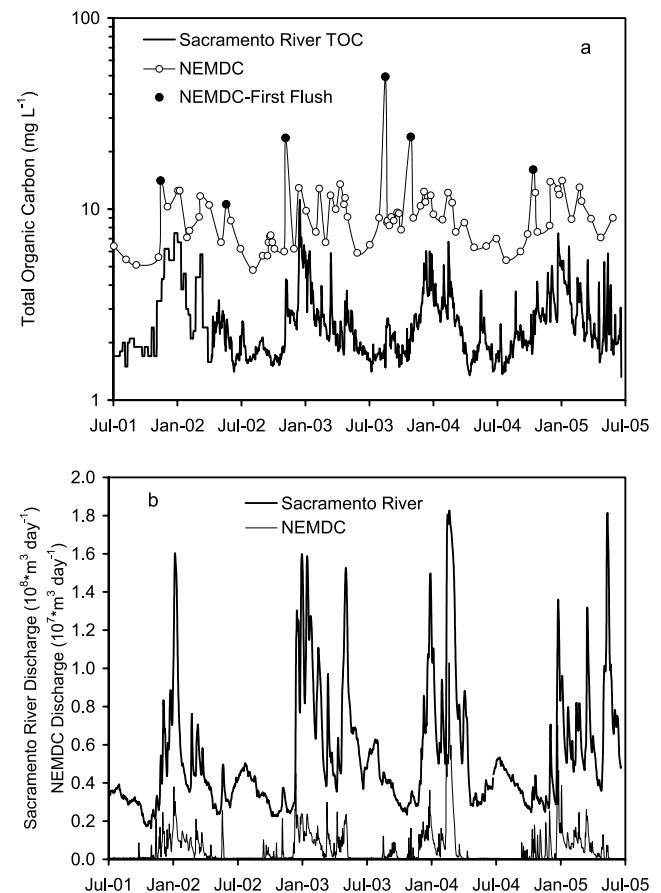
Figure 3. Measured TOC concentrations (panel a) and daily discharge (panel b) for NEMDC and the Sacramento River from 1 July 2001 through 30 June 2005. In panel a, first flush storms are denoted as solid circles and the online TOC measurements are the solid black line.

Table 2. Summary of Equations and Algorithms Used to Predict TOC Concentrations or Loads at NEMDC, the Sacramento River and Sacramento Regional Wastewater Treatment Plant (SRWTP)

Site and Method	Equation or Algorithm to Predict TOC Concentration or Load
NEMDC – Worked record	Extrapolation of chemistry to mid-point between samples or to most recent discharge change
NEMDC – Beale's ratio estimator on four strata	For $Q \leq 5.7$ m^3s^{-1}: $TOC_{conc} = 7.78$ mg L^{-1}
	For $Q > 5.7$ & ≤ 13.6: $TOC_{conc} = 9.07$ mg L^{-1}
	For $Q > 13.6$ & ≤ 21.4: $TOC_{conc} = 10.7$ mg L^{-1}
	For $Q < 21.4$ m^3s^{-1}: $TOC_{conc} = 12.3$ mg L^{-1}
NEMDC – Non-linear regression	$TOC_{conc} = 3.01 + [1.19 * \ln(Q)]$
NEMDC – LOADest[a]	$\ln TOC_{load} = 8.07 + 1.13 * LnQ + 0.059$ dt
NEMDC – First flush storms	$TOC_{conc} = 48.8 * Q^{-1.21}$
Sacramento River – Worked record	Mean daily TOC_{conc} computed from real-time and grab sample measurements at Hood Water Quality Station
SRWTP missing flows	$Q = 134, 206 * $ (Daily rainfall) $+ 610, 971$
SRWTP loads - LOADest[a]	$\ln TOC_{load} = 9.68 + 0.953*LnQ + 0.370*LnQ^2$
	$+ 0.068*Sin(2\pi$ dt$) + 0.012*Cos(2\pi$ dt$)$
	$+ 0.129*dt + -0.031*dt^2$

Q = mean daily discharge in m^3 s^{-1} and daily rainfall is in cm.

[a]$LnQ = \ln(Q) - $ center of $\ln(Q)$ and dt = decimal time $-$ center of decimal time.

prior to computing the estimators. The four flow strata used were: <5.7, $5.7 \geq <13.6$, $13.6 \geq <21.4$ and ≥ 21.4 m^3s^{-1}. In hydrologic terms these classes define four identifiable flow regimes within the NEMDC watershed: 1) base flow, 2) periods with agricultural runoff or small rain events (<1 cm), 3) moderate size rain events ($\sim 1-2$ cm of precipitation) and 4) large rain events (>2 cm). We performed an ANOVA on ranks (Freidman's method) followed by Dunn's multiple comparison test which demonstrated that mean TOC concentration for the four strata were different at the $p < 0.01$ level (Table 2).

[22] The final two methods employed to compute TOC loads at NEMDC were non-linear regression estimators. In the first, a logarithmic equation was fit to the discharge-concentration data to model daily mean TOC concentration on the basis of discharge (Table 2). This model broadly captured the clockwise hysteresis pattern observed between discharge and TOC concentration at NEMDC (Figure 2a). The log-model had an adjusted r^2 value of 0.63 and all regression coefficients were significant at $p < 0.01$ level.

[23] The second regression model was developed using the USGS FORTRAN program, LOAD estimator (LOADest) [*Runkel et al.*, 2004]. LOADest routines fit a non-linear regression model of constituent load using discharge, decimal time, and additional user-specified data as predictive variables. The formulated regression model was then used to compute loads over daily intervals. Calibration and estimation within LOADest were based on adjusted maximum likelihood estimation (AMLE) since regression residuals for NEMDC were normally distributed. The general form of the best fit equation describing the relationship between TOC load and discharge and time was:

$$\ln L = a_0 + a_1 \cdot \ln Q + a_2 dtime \qquad (2)$$

where, $\ln L = \ln$ TOC load in kg per day; $\ln Q = \ln(Q) -$ center of $\ln(Q)$; dtime = decimal time $-$ center of decimal time and a_0, a_1 and a_2 are model coefficients. Computation of loads was complicated by retransformation bias (i.e., exponentiation of equation 2), however, the LOADest

software corrected for this bias by introducing bias correction factors for the calculation of instantaneous load. Bias in load computations due to multicollinearity between the explanatory variables was also corrected by subtracting the center of the calibration data for discharge and decimal time respectively [*Runkel et al.*, 2004].

2.6. First Flush Storm Modeling

[24] On six dates between 2001 and 2005, spikes in TOC concentration were observed at NEMDC during rainfall events (Figure 3a and b). For these six storms, runoff was elevated above base flow for an average of 4.8 days (range $3-7$ days). TOC concentration during the events ranged from 10.6 to 49.3 mg L^{-1} during the first three days of rainfall-runoff generation and then returned to pre-event levels. The characteristics of these first-flush storms included an antecedent period without rainfall of at least 30 days and rainfall rates sufficient to induce a discharge increase of >10 m^3s^{-1}. The majority of first flush storms occurred in the autumn following long summers without rainfall, but first flush storms were also observed during the summer of 2003 and spring of 2002. There was a marginally significant, inverse relationship between discharge and TOC concentration for these storms (adjusted $r^2 = 0.54$; $p = 0.1$ for slope of line and $p = 0.01$ for intercept). A much stronger exponential decay relationship was found between TOC concentration and elapsed time during the runoff event (Figure 2b, adjusted $r^2 = 0.92$; $p < 0.001$ for both equation coefficients). Using this exponential decay model (Table 2) we computed daily mean TOC concentration during the first three days of first flush storms and multiplied by discharge to yield TOC load on these days. While several other first flush events probably occurred during the study period, we restricted use of the first flush model to the 18 days when water samples confirmed a first flush condition at NEMDC.

2.7. Estimation of TOC Loading From Metropolitan Sacramento

[25] To evaluate potential impacts of urban TOC sources on downstream Sacramento River TOC loads, the areal
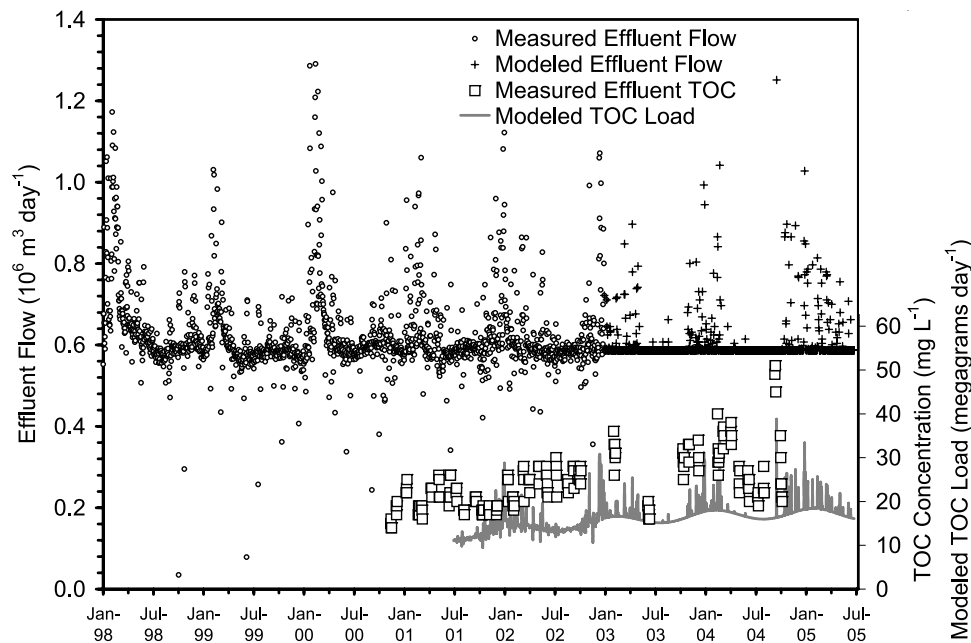
Figure 4. Flow and TOC characteristics of the Sacramento Regional Wastewater Treatment Plant (SRWTP) from 1998–2005. Measured flow data from 1998–2003 are denoted by open circles. Modeled flow data are shown as + signs; owing to close spacing the + signs appear as a solid black line. Measured TOC concentrations are denoted with open squares and modeled TOC loads in effluent are shown as a solid gray line. Raw data are from *Tetra Tech Inc.* [2006].

yield of TOC computed for the NEMDC watershed (i.e., kg TOC km^{-2} day^{-1}) was upscaled to the entire SMA to estimate Sacramento non-point loading. The NEMDC watershed drains 466 km^2 of the 1,424 km^2 SMA, but has about double the percentage of urbanized land relative to the SMA (Table 1). Given the lower percentage of urbanization in the overall SMA, we used an areal TOC yield of 50% of that in the NEMDC watershed to provide a conservative estimate of Sacramento non-point TOC flux:

Daily Sacramento non-point loading

$$= \left[466 \text{ km}^2 * N \text{ kg TOC km}^{-2} \text{ day}^{-1}\right]$$
$$+ \left[958 \text{ km}^2 * \tfrac{1}{2} N \text{ kgTOC km}^{-2} \text{ day}^{-1}\right] \qquad (3)$$

where, N equals daily areal yield of TOC from the NEMDC watershed.

[26] Total urban loading from the SMA was computed as the sum of Sacramento non-point load (equation (3)) and TOC in effluent from the Sacramento Regional Wastewater Treatment Plant (SRWTP). The SRWTP is the largest inland treated wastewater discharge in California and treats domestic and industrial wastes as well as street runoff from the SMA. From 1998–2003 the SRWTP discharged an average of about 7 $m^3 s^{-1}$ ($\sim$6 × 10^5 m^3 day^{-1}) to the Sacramento River about 24 km downstream of the NEMDC confluence and 13 km upstream of the Hood Station [*Tetra Tech Inc.*, 2006]. The median effluent TOC concentration was 23 mg L^{-1} during this same period [*Tetra Tech Inc.*, 2006]. Estimating daily TOC loading from the SRWTP was complicated by two issues: 1) no effluent flow data were available after December 2002 and 2) no chemistry data were available after October 2004 (Figure 4). To overcome these data limitations we modeled effluent flow as a function of rainfall (Table 2). Since the SRWTP is a combined sewer system, it receives regular daily input of sewage (ca. 7 $m^3 s^{-1}$) and additional influent from surface runoff during rain events. From observations of the response of effluent flow to rainfall in downtown Sacramento we fit a linear model to describe the increase in effluent flow during rain events ($r^2 = 0.4$). Because of storage effects, peaks in flow lagged peak rainfall rates by 1 day. Using this model along with rainfall records and assumed base flow discharge of 6.1 × 10^5 m^3 day^{-1} we created a synthetic effluent discharge record for SRWTP running from January 2003 through June 2005 (Figure 4). Daily TOC loads were then modeled using LOADest software using a calibration data set of 185 pairs of TOC concentration and discharge data (Figure 4; Table 2).

3. Results

3.1. Discharge and Chemistry Patterns

[27] Precipitation during the study period ranged from 80–106% of normal in the Sacramento River basin. Because of the Mediterranean climate of California, most precipitation falls during November to April with the exception of infrequent summer thunderstorms in years with strong monsoonal weather patterns. Discharge in NEMDC and the Sacramento River follow this general pattern although delayed mountain snowmelt, water storage and irrigation operations tend to compress the range of annual flows. Peak daily discharges at NEMDC ranged from 0.3 to 1.0 × 10^7 m^3 day^{-1} during years 2002–2005 and from 1.5 to 1.8 × 10^8 m^3 day^{-1} in the Sacramento River (Figure 3b). On a monthly basis, discharge from NEMDC contributed from 0.1 to 3% of the flow in the Sacramento River.
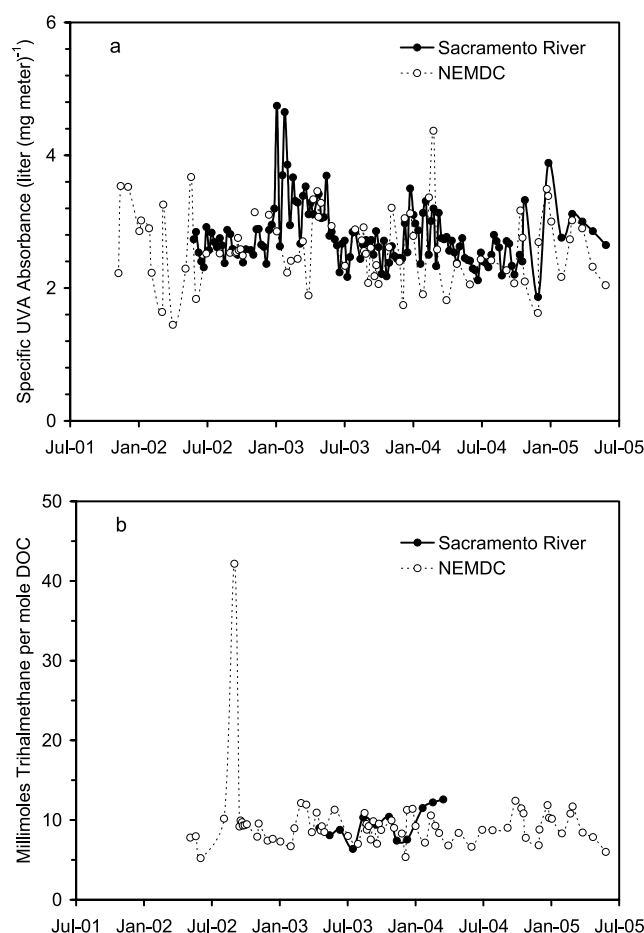
Figure 5. Specific UVA-254 absorbance (panel a) and specific total trihalomethane formation potential for NEMDC and the Sacramento River from 1 July 2001 through 30 June 2005.

[28] TOC concentrations at NEMDC ranged from 4 to 49 mg L^{-1} and were 4 to 20 times greater than TOC concentrations in the Sacramento River on the same dates (range 1–11 mg L^{-1}; Figure 3a). Peak TOC concentrations occurred during the winter months in the Sacramento River. In contrast, TOC levels at NEMDC were highest during first flush storms which were most frequent in the autumn. There was modest coherence between TOC concentrations in NEMDC and the Sacramento River; (Pearson Product Moment Correlation = 0.6; p < 0.001).

[29] SRTWP effluent discharges varied from about 0.04 to 1.24×10^6 m^3 day^{-1}, but were most frequently between 0.52 to 0.64×10^6 m^3 day^{-1} [*Tetra Tech Inc.*, 2006]. Peaks in effluent volume occurred during large rain events in the SMA and lasted up to one week. During 2000–2004, TOC concentrations in effluent ranged from about 15 to 50 mg L^{-1} and there was a significant increase in TOC concentrations with time (strength of correlation by Kendall tau = 0.4, p < 0.001; slope $\neq$ 0 by t-statistic, p < 0.001) [*Tetra Tech Inc.*, 2006].

[30] Organic carbon reactivity with chlorine at NEMDC and the Sacramento River was assessed by two measures: aromaticity as measured by specific UVA absorbance (SUVA) and specific trihalomethane formation potential

(STHMFP). No SUVA or STHMFP data were available for SRWTP effluent samples. STHMFP in the Sacramento River were measured only from April 2002 until April 2003. With the exception of a few days in September 2002 and January 2003, there was little difference in the SUVA or STHMFP of DOC at NEMDC and the Sacramento River. SUVA values typically varied between 2 and 4 liter (mg DOC meter)$^{-1}$ and STHMFP was usually between 5 to 12 millimoles THM (mole DOC)$^{-1}$ (Figure 5). Higher SUVA values during the winter of 2002–2003 in the Sacramento River were associated with a modest flood. The spike in STHMFP at NEMDC in fall 2002 was not associated with a rainfall-runoff event or any change in TOC concentration and may have resulted from analytical error.

3.2. Non-Point TOC-Load Modeling and Error Analysis

[31] The following nomenclature will be used when referring to urban TOC loads: (1) NEMDC load = non-point TOC loads from the NEMDC watershed, (2) SRWTP load = point TOC loads from the Sacramento Regional Water Treatment Plant, (3) Sacramento non-point load = sum of measured NEMDC non-point load plus estimated non-point load from remaining Sacramento Metropolitan Area (see section 2.7), and (4) Total urban load = sum of all non-point and point loads from the Sacramento Metropolitan Area. In addition, TOC loads in the Sacramento River at Hood Station will be referred to as Sacramento River load.

[32] NEMDC TOC loading was computed on a daily time step from continuous measurements of discharge and periodic chemical samples by the four previously described computational methods. During most months there was good agreement among the four methods (Figure 6a). Loads varied from about 4.3 to 1134 megagrams per month with highest loads occurring during December to February. Minimum loads occurred during the summer months.

[33] Using propagation of error techniques, we estimated the error in loading for each of the four methods [*Sokal and Rohlf*, 1994]; (Table 3). Total uncertainty in annual fluxes of TOC at NEMDC ranged from 25 to 31%. All four methods produced annual estimates of TOC yields that were within ±13% (Table 4). An ANOVA demonstrated no significant differences (p = 0.99) in the mean annual TOC yield computed by the four methods. Differences in annual TOC loads were <10% among the ratio and regression methods (Figure 6a). In contrast, loads computed by the worked record method differed by 30–40% from the ratio and regression methods during seven months (Figure 6a). This disagreement likely occurred because either too few or too many grab samples were collected during the month. When only a single water sample was collected during the month and the sample had unusually high or low TOC concentration, this skewed the extrapolated estimates of daily TOC concentration. In months with 4–5 grab samples, the worked record approach, most likely, better captured the true variability in TOC concentrations that occurred.

[34] Effluent from the SRWTP supplied between 350 to 550 megagrams of TOC to the Sacramento River on a monthly basis (Figure 6a). Month to month variation was relatively low relative to NEMDC load, but through time, there was a gradual and statistically significant (p < 0.01) increase in SRWTP loading due to increasing TOC concen-
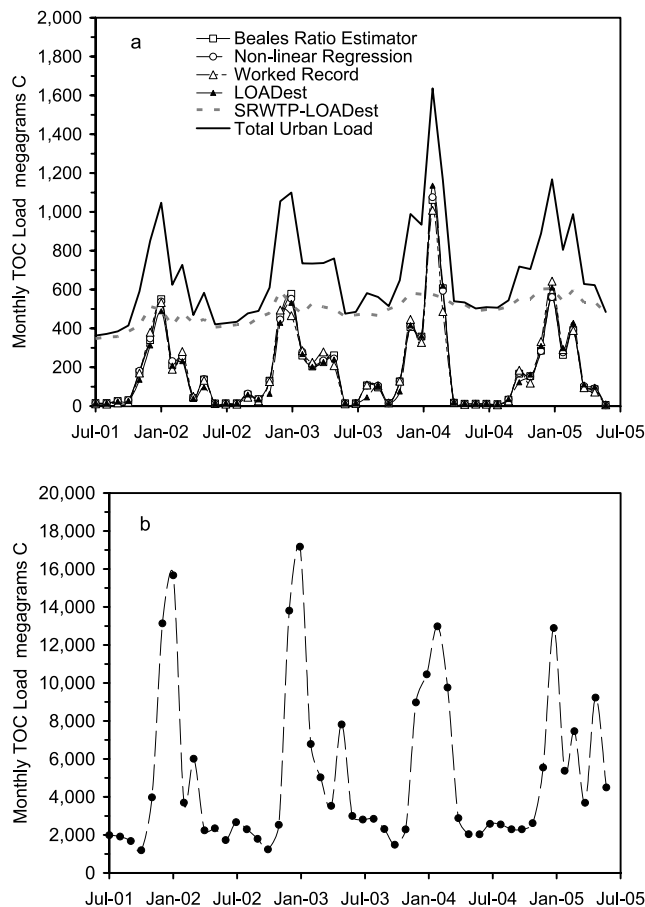
Figure 6. Panel a: Monthly TOC loads at NEMDC computed by four different methods, along with SRWTP loads (dashed line) and total urban TOC loading from Sacramento (solid line) computed using equation 3. Panel b: Monthly TOC loads in the Sacramento River.

trations in effluent. We estimate that the error in annual TOC loading from the SRWTP was 21% (Table 3).

[35] Total urban loading from the SMA was computed from the sum of Sacramento non-point loads (using Beale's ratio estimates for NEMDC and equation (3)) and SRWTP loads. Maximum total urban loading to the Sacramento River ranged from 1000 to 1600 megagrams TOC per month (Figure 6a) and occurred in January of each year. Minimum total urban loading occurred in the early summer and ranged from 400 to 500 megagrams TOC per month. Errors in total urban loads include the combined error for point and non-point loads and were on the order of 30–35%.

[36] Monthly loads in the Sacramento River during base flow conditions were between 1000 and 3000 megagrams TOC per month (Figure 6b). River loads peaked in January and varied from 13,000 to 17,000 megagrams TOC per month. Estimated error in annual Sacramento River TOC loads was 14% (see Table 3; sampling error was computed by bootstrapping).

3.3. Ratios of Urban TOC Loads to Sacramento River TOC Loads

[37] We evaluated the magnitude of total urban load and its components to loads in the Sacramento River on three timescales: annual, monthly and daily (Table 5). For annual TOC loads in years 2002–2005, the ratio of total urban load to Sacramento River loads varied from 0.15 to 0.20. For Sacramento non-point load, the average ratio was 0.07 and for the SRTWP the average ratio was 0.10.

[38] For monthly and daily contributions we ranked and computed percentiles for ratios of total urban load (and its components) to Sacramento River TOC loads (Table 5). At the 10th percentile level, monthly ratios for Sacramento non-point, SRWTP and total urban load were 0.01, 0.03 and 0.09 respectively. At the 50th percentile level (i.e., where half of the monthly contributions were lower) ratios were 0.07, 0.12 and 0.17, respectively. The 90th and 99th percentile values describe the top 10% and 1% of the urban:river TOC ratios. There were 4 months and 1 month, respectively, where total urban load equaled 26% and 34% of Sacramento River loads.

[39] At a daily time step, the 90th and 99th percentile values for the ratio of total urban TOC load to Sacramento load were 0.38 and 0.80 respectively (Table 5). Maximal daily ratios of total urban:river TOC loads exhibited a regular annual pattern of peaks in the spring (March and April) and minima in the summer (July and August;

Table 3. Derivation of Errors in Annual Flux Estimates at NEMDC, the Sacramento River and the Sacramento Regional Water Treatment Plant (SRWTP)

Site and Model	Analytical Error	Sampling or Model Error[a]	Discharge Error	Total Uncertainty in Annual Flux
NEMDC – Worked record	20%	9.5%	15%	27%
NEMDC – Beale's ratio estimator	20%	4.9%	15%	25%
NEMDC – Non-linear regression	20%	16.9%	15%	30%
NEMDC – LOADest[b]	20%	2.5%	15%	25%
NEMDC – First flush storms	20%	1.8%	15%	25%
Sacramento River – Worked record[c]	10%	3.0%	10%	14%
SRWTP - LOADest[b]	20%	3.3%	5%	21%

Total uncertainty in annual flux was estimated as the square-root of the quadratic sum of component errors for fluxes, i.e., analytical error, discharge error and sampling or model error [*Sokal and Rohlf*, 1994].

[a]Errors estimated from bootstrapping of annual TOC data (worked records and Beale's strata) or from standard errors derived from model fits (Non-linear regression, LOADest and first flush storms).

[b]Model error is for TOC load.

[c]TOC analytical error from *Sickman et al.* [2005]; Discharge error from *Freibel et al.* [2004].

Table 4. Organic Carbon Yield for the NEMDC Watershed Computed by Four Methods and for the Sacramento River Basin at Hood[a]

| | NEMDC | | | | Sacramento River (this study) | Sacramento River at Freeport 1995–1998 | Arcade Creek 1995–1998 |
Year	Worked Record	Beale's Ratio Estimator	Log- Regression	LOADest			
2001–2002	38.8	38.6	39.3	34.3	9.33		
2002–2003	47.0	48.5	48.0	44.9	11.4		
2003–2004	57.5	60.8	61.0	60.6	10.2		
2004–2005	46.7	44.3	44.8	47.3	10.3		
2001–2005 Mean	47.5	48.1	48.3	46.8	10.3		
Long-term Averages		Mean = 47.7				17	121

[a]Also shown are long-term average of yields for organic carbon for the Sacramento River Basin (1995–1998) and Arcade Creek Watershed (1995–1998) from *Saleh et al.*[2003]. Units are kg ha^{-1} yr^{-1}.

Figure 7a). On days with first flush storms (indicated by diamond symbols in Figure 7b), total urban loading approximated TOC loads in the Sacramento River (Figure 7b). The one week moving average of the ratio of daily Sacramento non-point load to Sacramento river load typically varied between 0.01 and 0.20. The one week moving average of the ratio of total urban load to river load varied between 0.10 and 0.50.

4. Discussion

4.1. Urban Contributions to Sacramento River TOC and DBP Loads
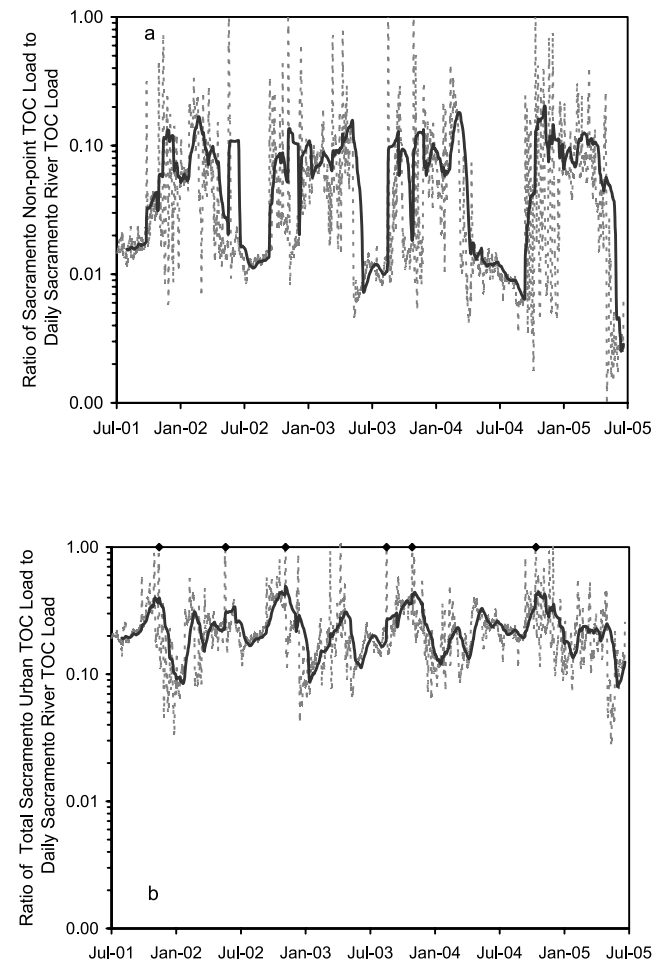
[40] For more than a century, the Sacramento River Basin has been undergoing landuse alteration. Initially, changes were dominated by conversion of grasslands and wetlands to agriculture. Coupled with damning of major rivers and introduction of non-native clams, these alterations have strongly influenced organic carbon loading to and cycling

Table 5. Frequency Distribution Ordered by Percentiles and Years of the Daily, Monthly and Annual Ratio of Non-Point, Point and Total Sacramento Urban TOC Load to Sacramento River TOC Load[a]

| | Daily Fractions | | | | |
UrbanTOC source	10th	50th	75th	90th	99th
Non-point	0.01	0.02	0.07	0.15	0.57
Point	0.04	0.17	0.22	0.29	0.40
Total	0.10	0.20	0.27	0.38	0.80
	Monthly Fractions				
	10th	50th	75th	90th	99th
Non-point	0.01	0.07	0.09	0.12	0.16
Point	0.03	0.12	0.15	0.19	0.29
Total	0.09	0.17	0.22	0.26	0.34
	Annual Fractions				
	2002	2003	2004	2005	Mean
Non-point	0.06	0.07	0.09	0.07	0.07
Point	0.09	0.09	0.10	0.11	0.10
Total	0.16	0.15	0.20	0.17	0.17

[a]The number of observations for the yearly, monthly and daily fractions is 4 a, 48 months and 1461 days, respectively (1 July 2001 through 30 June 2005).

within the Sacramento-San Joaquin Delta [*Jassby and Cloern*, 2000]. Over the last several decades, conversion of agricultural lands to urban uses has accelerated with growing population in the Central Valley of California. The impacts of urbanization on the quantity and chemical

Figure 7. Ratio of Sacramento non-point (a) and total urban TOC contribution (b) to TOC loads in the Sacramento River from 1 July 2001 through 30 June 2005. The black line is the one-week moving average and the diamond symbols in the lower panel show the timing of observed first flush storms.

composition of organic matter inputs to fluvial systems are poorly understood, but several recent studies suggest that urban landscapes have measurable influence on TOC loads in rivers. For the Sacramento River, *Saleh et al.* [2003] estimated that 24% of the Sacramento River DOC load at Freeport during May 1998 was derived from unidentified inputs between Verona and Freeport; this river reach receives runoff from the SMA and adjacent agricultural lands. Additional studies in the United States and Europe have found relationships between the degree of urbanization within catchments and DOC levels in surface runoff during storm events [*Hook and Yeakley*, 2005], and long-term changes in DOC concentrations in lakes [*Muller et al.*, 1998].

[41] Using continuous flow data, regular chemical sampling of NEMDC, landuse patterns in the SMA and published flows and TOC from the SRWTP, we estimated the rate of TOC loading from urban sources to the Sacramento River. We compared these loading rates to TOC loads in the Sacramento River derived from real-time measurements of TOC concentrations and continuous discharge measurements at Hood Station, located 32 km downriver from Sacramento. In interpreting these comparisons we propose that the ratios of urban:river TOC loads equal the actual percentage of Sacramento TOC load derived from point and non-point sources in the SMA (Table 5 and Figure 7). While TOC is not a strictly conservative constituent of rivers, we believe there is little opportunity for biogeochemical transformations to alter the mass of TOC in the river between Sacramento and Hood Station. During base flow, mean flow velocity in the Sacramento River at Freeport was 0.1 to 0.3 m s^{-1} and velocity exceeded 1.5 m s^{-1} during high flows [*Ruhl and DeRose*, 2004]. Mean traveltime between Sacramento and Hood Station, therefore, ranges from about 2.5 days to 6 h. Previous studies of the mineralization potential organic matter in Delta waters have demonstrated that less than 15% of DOC and 33% of POC are bioavailable to aquatic heterotrophs over 28-day aerobic incubations [*Sobczak et al.*, 2002].

[42] On an annual basis, we estimate that about 17% of the load of TOC in the Sacramento River at Hood was derived from Sacramento urban sources during years 2002–2005.; about 10% was derived from the SRWTP and 7% came from non-point runoff. The uncertainty in these estimates is ±30–35%, and we have been cautious in computing non-point loading through conservative upscaling of NEMDC areal yield and underestimation of first flush storms. Thus on an annual basis, an appreciable amount of TOC contributed by the SMA reaches the Delta. At shorter time-scales, the impact of TOC loading from urban runoff on the Sacramento River increased. About 50% of the time, total urban load made up 17–20% of the monthly and daily TOC load in the Sacramento River at Hood (Table 5). On 10% of days, total urban load constituted 38% or more of the Sacramento River TOC load at Hood and during first flush storms, greater than 80% of the river TOC load came from urban sources. During every first-flush storm at NEMDC, we observed an increase in Sacramento River TOC concentrations at Hood of between 25–100%. Maximum urban contributions occurred on days with first flush storms in the summer and autumn when Sacramento River flows were low.

[43] While TOC concentrations in urban runoff were usually 4–20 times greater than in the Sacramento River, the potential reactivity of the non-point organic matter with chlorine was similar to that in the Sacramento River. At both sites SUVA typically ranged from 2 to 4 L (mg DOC meter)$^{-1}$ and DBP formation potential varied from 5 to 12 millimoles THM (mole DOC)$^{-1}$ (Figure 5). In relationship to agricultural drainage, Sacramento non-point urban runoff has slightly lower DBP formation potential per mole DOC (typical agricultural drainage range = 9–13 millimoles THM (mole DOC)$^{-1}$; J. Sickman and C. DiGiorgio, unpublished data) and slightly higher SUVA (typical agricultural drain range = 4–6 L (mg DOC meter)$^{-1}$)) (J. Sickman and C. DiGiorgio, unpublished data). Furthermore, our qualitative measurements of DOC reactivity with chlorine do not indicate any fundamental difference in the characteristics of DOC in first flush storms versus other rain events. While gross STHMFP was higher in first flush samples, these differences disappeared when normalized to the mass of DOC in the sample. Our findings suggest that contributions of DBP precursors from Sacramento non-point sources to Delta DBP precursor loads are directly proportional to their TOC mass contributions. Since we lack SUVA and STHMFP for the SRWTP it is difficult to speculate on the reactivity of TOC in wastewater effluents entering the Sacramento River. However, data for effluents from other wastewater systems (secondary treatment) suggests similar SUVA and STHMFP values and a positive relationships between THMFP and TOC concentrations [*Sirivedhin and Gray*, 2005; *Chu et al.*, 2002].

4.2. Urbanization and Watershed TOC Yields

[44] On an areal basis, TOC yield from the NEMDC watershed averaged 47.7 kg ha^{-1} yr^{-1} during years 2002–2005 which had near normal precipitation amounts. This yield is more than 4-times greater than yield from the entire Sacramento River Basin during the same years, 10.3 kg ha^{-1} yr^{-1}, but less than one-third of the yield of TOC from the highly urbanized Arcade Creek watershed measured during a 4-a period when precipitation averaged 156% of normal (121 kg ha^{-1} yr^{-1}; Table 4). To put these rates in context, the TOC yield from the Sacramento River Basin is similar to TOC yields from cool grassland biomes (<10 kg ha^{-1} yr^{-1}; *Aitkenhead and McDowell*, [2000]). In contrast, NEMDC yields are similar to coniferous forest biomes with rates of 15–75 kg ha^{-1} yr^{-1}. Yields of >75 kg ha^{-1} yr^{-1} are uncommon in large rivers and are primarily restricted to peatlands, tropical forests and high latitude mixed forests. TOC yield from the Arcade Creek watershed during 1995–1998 was, in fact, equal to the measured yield of TOC in the Rio Negro River of Brazil [*Richey et al.*, 1990]. From the perspective of riverine ecosystems and terrestrial organic matter inputs, ongoing urbanization of the Sacramento River Basin represents a shift from a grassland biome to one more similar to a forest ecosystem.

[45] About 80% of the Sacramento River watershed is in an undisturbed condition and only ~3% is urbanized. In contrast, the NEMDC watershed is 59% urbanized and the Arcade Creek watershed is almost completely urbanized. These data suggest that there is a positive relationship between areal TOC yield and the degree of urbanization in the Sacramento River Basin. This finding is consistent

with numerous studies that have shown that concentrations and loads of pollutants in surface runoff increase with urbanization [*Arienzo et al.*, 2001; *Vernberg et al.*, 1996]. *Scheuler* [2006] found that water quality can be affected by as little as 10% impervious cover and other studies suggest that drinking water quality is diminished at 25% impervious cover [*Center for Watershed Protection*, 2003].

4.3. Mechanisms of TOC Generation in Urban Watersheds

[46] There are several potential mechanisms to explain why urbanization increases TOC loading to rivers. The most obvious reason is wastewater discharge. Untreated sewage has TOC concentrations of several grams C L^{-1} which is reduced to a few tens of mg L^{-1} by sedimentation, aeration and microbial action. Even with treatment, TOC levels in effluent waters are commonly much higher than in receiving waters [*Viessman and Hammer*, 1996; *Westerhoff and Anning*, 2000; this study]. Non-point TOC loads are also elevated in urbanized watersheds relative to less disturbed landscapes. One reason might be increased water yield. Because of impervious surfaces, rainfall-runoff responses from urban landscapes exhibit more rapid rise to peak discharge, higher peak flows and quicker recovery to base flow conditions [*Singh*, 1997]. Greater hydrologic response to rainfall results in higher runoff coefficients (i.e., depth of runoff divided by depth of precipitation) and coupled with irrigation of landscaping suggests that areal runoff increases with urbanization. However, increases in the volume of runoff do not completely explain higher TOC yields in Sacramento. As observed at NEMDC, TOC concentrations are often many times higher than in runoff from undisturbed watersheds, suggesting there are additional sources of organic matter in urban environments relative to undisturbed landscapes in the Central Valley of California.

[47] Previous studies have detected a large number of organic contaminants in non-point runoff from California urban areas and elsewhere, including pesticides [*Amweg et al.*, 2006; *Crawford*, 2001; *Larson et al.*, 1995; *Soller et al.*, 2005], poly aromatic hydrocarbons derived from fuel combustion, asphalt and roofing materials [*Menzie et al.*, 2002; *Stein et al.*, 2006; *Van Metre and Mahler*, 2003] and surfactants [*City of Encinitas*, 2002]. However, based on these published studies, petroleum-based pollutants are found in $\mu g\ L^{-1}$ concentrations in non-point urban runoff. DOC levels at NEMDC during base flow were >3 mg L^{-1} and during first flush storms ranged from 10.6 to 49.3 mg L^{-1} suggesting that petroleum products could make up only a small fraction of bulk DOC loads.

[48] Additional organic matter sources in urban runoff may include partially decomposed vegetation that accumulates on catchment surfaces during the long, dry summers; this material may be washed into urban streams during the wet season. The urban forest within the SMA is extensive with an estimated 1.7×10^6 trees, which store upwards of 360 megagrams C ha^{-1} and represent a large pool of potentially mobile organic matter [*Nowak and Crane*, 2002]. Particulate organic carbon (POC) was not separately measured at NEMDC, but can be approximated by the difference between TOC and DOC. In most samples, POC levels were between 1 to 5 mg L^{-1}, however, during first flush storms concentrations could exceed 10 mg L^{-1},

indicating greater quantities of POC were washed into streams during intense rain events. Still, since the mean ratio of DOC:TOC in NEMDC samples was 0.75, neither hydrocarbon pollutants nor suspended particles account for the majority of the excess organic matter exported in Sacramento non-point runoff relative to less disturbed landscapes in the Sacramento River Basin.

[49] Instead, we hypothesize that soil organic matter is the primary source of DOC in Sacramento non-point runoff. Prior to large-scale development, much of the Sacramento Valley, including the site of the city of Sacramento, was covered by native annual grasslands and wetlands. Carbon storage in Mollisols (grassland soils) and Histosols (wetland soils) is substantial and exceeds organic carbon storage in more mesic soils typical of forested ecosystems (i.e., Alfisols and Spodosols) [*Stevenson and Cole*, 1999]. Widespread reductions in soil organic matter likely occurred during the 20th Century as grasslands were plowed and wetlands drained for agriculture in the Sacramento River Basin [*Guo and Gifford*, 2002; *Paustian et al.*, 1997]. Losses of soil organic matter likely continue as soils are "urbanized". Building and road construction result in continued disruption of soils, accelerating erosion and exposing soil organic matter to oxidizing conditions [*Deverel and Rojstaczer*, 1996]. Carbon mineralization in urban soils may be further enhanced by application of irrigation water and nitrogen fertilizers [*Koerner and Klopatek*, 2002; *Zhu et al.*, 2006]. Increased mineralization may also result from locally higher soil temperatures caused by urban heat-island effects associated with cities [*Peterson and Owen*, 2005].

[50] Additional information on the composition and chemical structure of TOC are needed to test the hypothesis that organic matter in non-point runoff from the SMA is primarily derived from soils. Radiocarbon measurements were performed on DOC isolated from NEMDC samples collected on two dates, 8 November 2002 and 28 April 2003. The November sample was from a first flush storm, but, other than elevated DOC concentration (22.0 mg L^{-1}), DOC in this sample had typical SUVA and STHMFP. The April sample (DOC = 11.5 mg L^{-1}) was collected after a small spring storm (1.8 cm) and also had normal SUVA and STHMFP. Thus these samples capture a wide range of the concentration and have reactivity with chlorine similar to the majority of NEMDC samples. The radiocarbon content of bulk DOC in these samples was 0.76 and 0.73 fraction modern carbon (fmc) with an inferred mean age of *ca.* 2000–2500 a. Radiocarbon content in co-collected samples of the Sacramento River and agricultural runoff from Delta islands had mean ^{14}C concentration of 0.85 ± 0.03 (s.e.) and 0.75 fmc ± 0.01 (s.e.) (J. Sickman and C. DiGiorgio, unpublished data). The age of bulk DOC in non-point runoff from Sacramento is similar to that in agricultural runoff where the DOC pool is known to be dominated by humic and fulvic acids originating from soils (*Fujii et al.*, 1998; J. Sickman and C. DiGiorgio, unpublished data). While it is possible that the same radiocarbon content of bulk DOC could result from a mixture of modern carbon sources such as plant leachates and very old sources derived from petrochemicals, this seems unlikely given the small variability in ^{14}C in the two NEMDC samples. One might also expect more ^{14}C-depleted DOC in the November 2002

sample given that petroleum-based chemicals exhibit first-flush behavior in other urban watersheds [*Soller et al.*, 2005]. We believe that the radiocarbon data provide evidence that soil organic matter makes up a large fraction of the bulk DOC in non-point runoff from the city of Sacramento. Furthermore, the data are evidence that losses of soil organic matter continue after agricultural soils are urbanized.

[51] Recent analyses of long-term records from the Hudson River (eastern U.S.) [*Findlay*, 2005], and the River Tees (United Kingdom, UK) [*Worrall and Burt*, 2004] indicate increasing DOC concentrations during the 20th Century. The DOC in these catchments is believed to be derived primarily from soils, but the mechanisms underlying increased DOC loads in these rivers are uncertain. In the case of the River Tees, increasing DOC loads were positively associated with climate change (higher air temperatures) and the incidence of severe drought which altered soil moisture and enzymatic controls on peat decomposition (i.e., the "Enzymatic Latch"; *Freeman et al.*, 2001b). DOC concentrations in the Hudson River have doubled since the late 1980s and this trend is attributed to a soil microbial response to elevated nitrogen deposition, resulting in greater losses of soil organic matter [*Findlay*, 2005]. In neither case was urbanization identified as a contributing factor to rising DOC levels, but in both watersheds population growth resulted in urbanization of agricultural lands.

[52] The combination of wastewater discharges and relatively high concentrations of TOC in non-point runoff produce high areal rates of TOC yield from urban area in comparison to undisturbed landscapes. Indeed, if SRWTP loads are added to Sacramento non-point loads, the effective yield of TOC from the SMA is 150 kg ha^{-1} yr^{-1}, which exceeds the yield from all 164 watersheds presented in *Aitkenhead and McDowell* [2000]. While large-scale climate forcing and regional effects of atmospheric deposition are likely affecting organic matter dynamics in river basins, our data suggest that urbanization should be carefully considered when examining long-term trends in DOC loads in rivers.

5. Conclusions

[53] Landuse change can alter the amount and chemical composition of organic matter entering riverine systems. These alterations, in turn, can affect downstream ecosystems and degrade drinking water quality. Urbanization of natural and agricultural lands is occurring in many regions of the United States, however there is little information on the effects of urbanization on TOC sources and loads to rivers. To fill this knowledge gap we determined the contribution of point and non-point TOC loads from the Sacramento Metropolitan Area to the Sacramento River and Sacramento-San Joaquin Delta during years 2002–2005. In addition, we made measurements of the radiocarbon content (age) of DOC, and its potential reactivity with chlorine (specific UV-A absorbance (SUVA) and specific trihalomethane formation potential (STHMFP)) to gain better understanding of urban DOC sources and fate.

[54] Median TOC concentrations in urban runoff from Sacramento were 4 to 20 times greater than in downstream

portions of the Sacramento River. The SUVA and STHMFP of DOC in non-point urban runoff were similar to that in the Sacramento River. On an annual basis, at least 17% of the TOC in the Sacramento River downstream of Sacramento came from urban runoff. Wastewater discharges made up about 60% of urban inputs to the Sacramento River with the balance coming from non-point runoff. At shorter timescales, urban runoff contributed a larger proportion of Sacramento River TOC loads: the 10th, 50th, 90th, and 99th percentile contributions of SMA sources to daily TOC load in the Sacramento River were 10%, 20%, 38%, and 80%, respectively. The effective TOC yield from the SMA was approximately 150 kg ha^{-1} yr^{-1} which is much higher than yields measured in rivers globally. This finding suggests that urbanization should be carefully considered when examining past trends in river chemistry and for modeling future impacts of urbanization on regional carbon balances. Radiocarbon dates for DOC in non-point runoff were > 2000 a suggesting that soil organic matter is the major source of DOC in non-point runoff from Sacramento.

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